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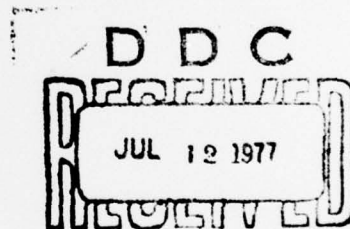
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CONFERENCE ON LUMINESCENCE PROCESSES IN CATHODE-RAY
TUBES AND LAMPS, WEYBRIDGE, SURREY, ENGLAND, MARCH 1977

JAMES H. SCHULMAN

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PHOSPHORS	ENERGY TRANSFER	RARE EARTH
ACTIVATORS	CATHODE-RAY TUBES	PHOSPHOR SURFACES
SENSITIZERS	X-RAY SCREENS	SURFACE STATES
ENERGY LOCALIZATION	CONCENTRATION QUENCHING	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This Europhysics study Conference on phosphors dealt with inorganic-impurity-activated phosphors used in cathode-ray tubes, fluorescent lamps, and x-ray screens. Most emphasis was given to the saturation effects in cathode-ray excitation of phosphors and the general problems of energy absorption, localization, transfer and emission in these phosphors.

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CONFERENCE ON LUMINESCENCE PROCESSES IN
CATHODE-RAY TUBES AND LAMPS,
WEYBRIDGE, SURREY, ENGLAND, MARCH 1977

This Europhysics Study Conference was held under the auspices of
the Institute of Physics on 29-31 March 1977 at the National College of
Food Technology, Weybridge, some 20 miles southwest of London. Roughly
half of the approximately 80 participants came from the UK, with the ma-
jor continental representation coming from Holland, France, and Germany.
The US was well represented by industrial scientists from the major com-
panies making lamp and cathode-ray tube phosphors, 10 Americans being
involved, while the Eastern Bloc countries were represented by one dele-
gate each from Czechoslovakia and the Soviet Union. The Conference chair-
man was L.A. Thomas (General Electric Company, Wembley).

The plan of the meeting was to make it something like a Gordon Con-
ference (albeit one that went on from morning till night without respite!).
Invited speakers reviewed the state of knowledge and current problems
on a number of preselected topics, and the participants then were given
ample opportunity for discussions from the floor. There was also plenty
of time for contributed papers, the so-called "mini-talks," which in one
session numbered up to 10. Brief abstracts of most of the principal talks
were provided in advance of the meeting.

In his opening remarks Thomas mentioned that the meeting subject was
chosen by the Physics in Industry Committee as a chance to bring together
basic and applied research, industrial and academic people, and physicists
and chemists. How well this objective was achieved I will conceal until
the last few paragraphs of this Report.

The opening speaker was the program chairman, Paul Dean of the Royal
Signals and Radar Establishment (RSRE, Malvern), who dealt with the prob-
lems of high cathode-ray tube (CRT) output, particularly saturation phe-
nomena. The light output of most phosphors tends to saturate with increas-
ing current density in the exciting electron beam within the range of
excitation densities used in CRT, thus limiting the attainable range of
brightness. Dean's talk was centered around experiments made by D.J.
Robbins of the RSRE to see whether the effect was due to saturation of
the ability of the activating impurity to "load and fire," the onset of
some higher order competing de-excitation mechanism, or to a perturbation
of the recombination kinetics of the charge carriers at high densities
of input power. The experiments were done with europium-activated yttrium
oxysulfide (Y_2O_2S:Eu), which is typical of rare-earth activated phosphors.
Rare-earth activators generally give sharp emission lines, originating
from transitions between sharp energy levels. The rare earths can be
incorporated into wide band-gap ceramic-like materials at high concentra-
tions without "concentration quenching" (the loss of luminescence efficiency

with increasing concentration of the activating impurity). Even these phosphors, however, suffer saturation effects under high intensity excitation in CRTs.

Dean first gave an account of cooperative experiments with the Ferranti Company in which the light output measurements were made on sealed-off CRTs containing (yttrium aluminum garnet) YAG:Tb,Gd phosphor. The Gd emission decreases with temperature in an almost linear fashion in the 0-100°C range, while the Tb emission does not decrease in this temperature range. The emission intensity of both activators was measured as a function of CR beam-current and both showed saturation. The temperature attained by the phosphors under high-current conditions could account for only a small fraction of the decrease in Gd emission and for none of the decrease in Tb emission, indicating that thermal quenching was not the mechanism of saturation in either activator.

In Robbins' experiments the ratio of two Eu emission lines could be used as an "internal thermometer" for Y_2O_2S:Eu. The 468-nm line of Eu (transition from the $^5D_2$ level) decreases with temperature and is nearly quenched at 400 K, while the emissions at 587 and 618 nm (transitions from $^5D_1$ and $^5D_0$ levels) are relatively independent of temperature. Robbins made observations on the time-dependence of the various emission lines at different current densities and with different methods of mounting of the phosphor powder on the substrate. The emission lines due to the temperature-sensitive and temperature-insensitive transmissions behaved similarly, again indicating that thermal quenching was not the mechanism of saturation. The time-dependence of brightness was eliminated when the phosphor mounting was changed from conventional support of the phosphor on conducting glass to the use of a conducting (epoxy plus silver) adhesive. This led Dean and Robbins to suggest that charging of the phosphor is important. Optical excitation of the phosphor alone was tried but did not give saturation at levels where the electron beam produced this phenomenon. Moreover, by application of an alternating field to a phosphor excited optically by a laser beam, the dc level of luminescence intensity could be modulated at twice the frequency of the field with the three lines of europium in the oxysulfide undergoing 16, 11, and 10% modulation (the largest modulation being of the $^5D_2$ line). Dean proposed some tentative models where surface charge could lead to either a quenching or an enhancement of luminescence.

In a question following his talk, Dean was asked whether secondary emission properties were important. These take place in 10^{-12} seconds, whereas the time-dependence in the brightness curves that Dean showed involves milliseconds. Dean pointed out that there are relaxation effects in an insulating phosphor which can be responsible for these long times.

G.O. Muller (Zentral Institut for Elecktronen Physik, Berlin) remarked that saturation under high optical excitation is not a common phenomenon.

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With lasers one can now achieve 10^{31} electron-hole pairs/cm^3-sec. Most materials stand these excitation intensities without irreversible changes because they are good phosphors at these high excitations. And at such high excitations one can saturate concentrations of 10^{19} cm^{-3} of impurities. This permits electron-hole recombination by pathways available in the host lattice, thus giving high "intrinsic" luminescence. This is apparently the case in CdS, the saturation of quenching-impurity levels causing an increase in luminescence efficiency. Saturation effects under cathode-ray excitation must therefore have a different cause, and surface effects are a reasonable explanation.

C.G.A. Hill (Levy West Laboratories, Enfield) in one of the mini-talks, described his attempts to obtain a current-modulated color CRT by using a blend of a sub-linear red phosphor and a super-linear green phosphor, both consisting of II-VI compounds (zinc-cadmium sulfides with various activators and "killer" centers). The super-linear phosphors used nickel as a killer with chlorine as a co-activator; the sub-linear ones were made with low concentrations of silver or copper activators. A reasonable degree of color modulation (red to green) was obtained over the range of current densities 0.1 to 100 μA/cm^2.

A.L.N. Stevels (Philips, Eindhoven) gave an invited paper on energy absorption and diffusion in phosphor hosts. This was a workmanlike and comprehensive review of the fundamentals of absorption by host lattices, sensitizers and activators, energy migration and energy transfer. The conclusion was that we are now able to do all sorts of intriguing things predictably with ultraviolet-excited phosphors, but that the problems are a lot more complex and our understanding is a lot less when cathode-ray and x-ray excitation are involved.

In one of the mini-papers which followed, W. Lehmann (Westinghouse, Pittsburgh) reported on an interesting (but useless) phosphor, CaO:Eu^{+3}. This phosphor was an attempt to substitute for Y_2O_3:Eu^{+3}, which would be the best red phosphor one could get for fluorescent lamps. Since the yttrium oxide is too expensive for this large-scale use, the possibility was explored of using europium-activated calcium oxide. This is a highly ionic material which requires some type of charge compensation for the trivalent europium activator. If alkali-ion is used as a charge compensator, the emission spectrum has components in the yellow, giving an undesirable emission spectrum. However, if "uncompensated" CaO:Eu^{+3} is made (compensation taking place by the formation of Ca^{+2}-ion vacancies), one gets the desired saturated red emission. The material is soft and is damaged by the grinding necessary for milling it into a lamp-phosphor powder. If the phosphor is fired at 1300-1400°C and quenched, the efficiency is as high as that of Y_2O_3:Eu. However, if it is refired at lower temperatures, the efficiency falls, a 1000°C firing dropping the efficiency to about 28%. From this Lehmann concluded that complex aggregates, consisting of Ca^{+2} vacancies near Eu^{+3} ions, produce radiationless transitions.

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However, in any case, the phosphor cannot be used inside a fluorescent lamp because of reaction of the CaO with traces of water and with other products of the glow discharge which poison it.

A. Bril (Philips, Eindhoven) surveyed the field of x-ray-excited phosphors. A number of new phosphors have been developed during the past years which are candidates for replacement of the traditional $CaWO_4$ and ZnCdS phosphors in fluoroscopic screens, intensifying screens and image intensifier tubes. Indeed CsI:Na has virtually replaced ZnCdS for the latter application. Other phosphors of interest are CsI:Tl, Gd_2O_2S:Tb, LaOBr:Tb, BaFCl:Eu, and Y_2O_2S:Tb.

A new technology (vapor deposition) is needed for the phosphor CsI:Na, developed in the late '60s [P. Brinckman, *Phys. Lett.* $\underline{15(4)}$, 305 (1965)], which has an emission band peaking near 4000 Å. Compared to screens made with powders of ZnCdS or $CaWO_4$, which give a material packing-density of 50%, one can achieve 100% packing-density with vapor-deposited CsI:Na. By introducing small cracks perpendicular to the deposited layer, one can also get better resolution than from the powder screens. By using standard film as a detector, CsI:Na gives 16 times the efficiency of detection and CsI:Tl gives 6 times the detection efficiency of $CaWO_4$ for 65 kV x-rays. The Na-activated salt is hygroscopic and can therefore be used only in vacuum devices, i.e., in intensifying tubes. The Tl-activated salt is less hygroscopic.

The rare-earth-activated phosphors mentioned above have line spectra. In general the Tb-activated phosphors with low concentration of activator give a blue emission and those with higher activator concentration give a visually green emission. Tb^{+3}-activated Gd_2O_2S and LaOBr are very promising, as is BaClF:Eu.

J.P. Galves (Thompson-CSF, St.-Egreve) followed with a paper on the formation of thick evaporated layers of CsI:Na for intensifying tubes, and the effects of bombardment, baking time, humidity and other factors on its luminescence efficiency. His conclusions were that Na^+ causes lattice defects (specifically I^- vacancies) in the host lattice and that the luminescence is connected with the presence of these anion vacancies. Color centers produced by cathode-ray bombardment act as killer centers for the luminescence. Post-evaporation heat treatment (1 hour at 400°C) makes the Na^+-ion concentration more homogeneous throughout the film and somehow reduces the problem of color-center formation under bombardment. When the evaporation is carried out in the presence of iodine, the luminescence is decreased.

D.J. Robbins (RSRE, Malvern) whose work had been referred to in Dean's opening lecture, reviewed the topic of energy localization and trapping effects at activators and sensitizers. Robbins pointed out that since gamma-ray, x-ray and cathode-ray excitation produce energetic electrons

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and holes in the phosphor lattice, efficient operation of a phosphor re-
quires efficient transfer of the electron-hole (e-h) recombination energy
to the impurity activators in the host lattice. For this to occur there
must be a low probability for e-h recombination by paths which compete
with the lattice activator transfer path; conversely, there must be a
strong interaction between the e-h excitation and the localized states
of the activator ions. Robbins' review emphasized the common feature
of such varied luminescent systems as organic molecular crystals, alkali
halide scintillators, and the ZnS phosphors, namely, the localization
of the host lattice excitation on some intermediate bound state as shown
in the accompanying figure.
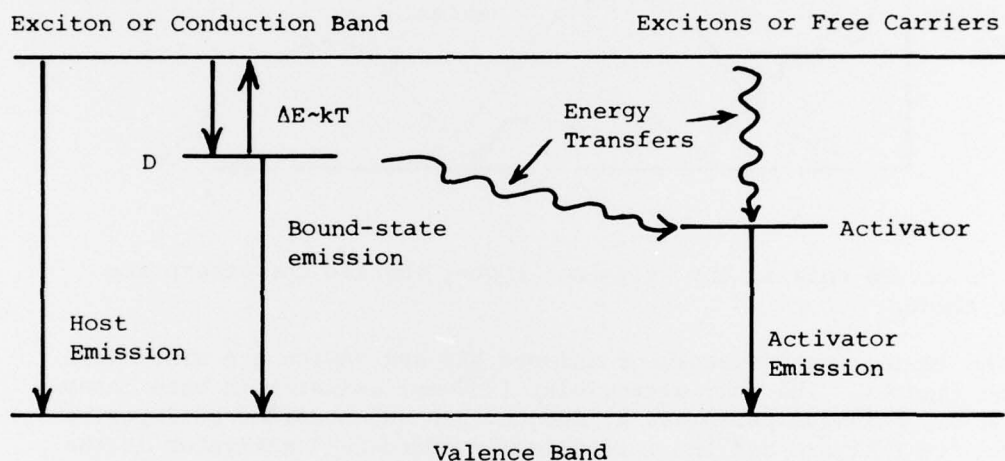
Transfer of this localized excitation to the activator can then take place
by a number of different mechanisms (diffusion or resonance transfer,
for example).

As a specific illustration Robbins described the results of RSRE stud-
ies on rare-earth-activated YAG. Gd-activated YAG shows a lower quantum
efficiency than the same host activated with Ce, Tb, or Eu. At higher
concentrations, these last three activators give phosphors with unit quan-
tum efficiency. They also give strong absorption bands in the neighbor-
hood of the host YAG absorption, whereas Gd has only weak absorption
in that region. (See accompanying figures.)
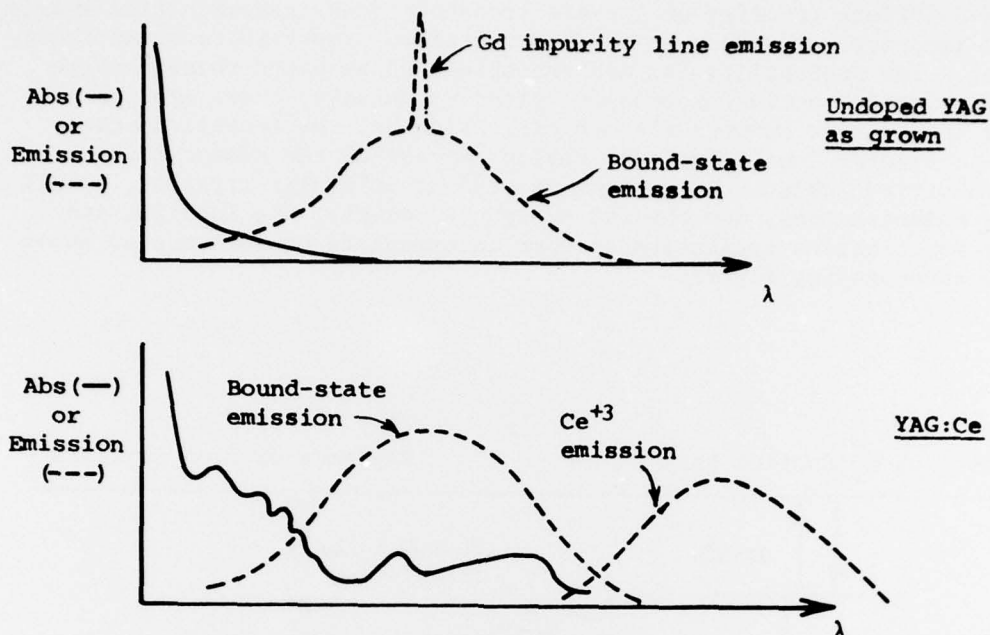
Also Gd occurs only in the trivalent state, whereas the others are multivalent.

The luminescence spectra of undoped YAG and YAG:Ce are also shown in the figures. The near-ultraviolet (337-mμ) emission in both cases is the YAG emission perturbed by defects, an uncontrolled Gd impurity in the first figure and the intentionally added Ce^{+3} activator in the second figure. (This defect-state emission, incidentally, is not a single band, as is found by studies of its time and wavelength dependence.) Transfer of the excitation energy from this rather complex defect state "D" to the Ce^{+3} activator can occur by either of the two processes illustrated in the figure below:

Lattice Excited State

Lattice Ground State
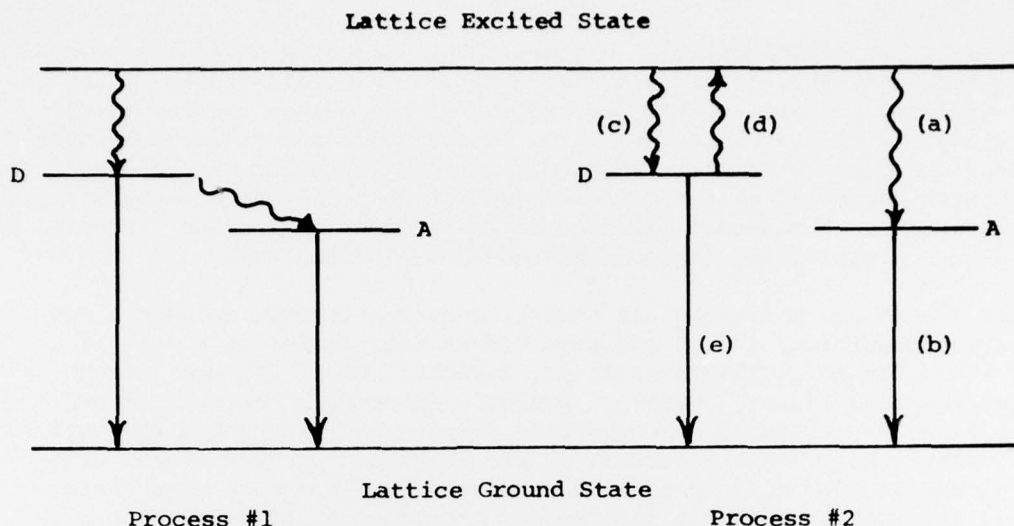
Process #1 Process #2

These processes can be differentiated by measurements of the temperature-
dependence of the luminescent emission. Measurements favor process (2).
The action of the state "D" as a recombination center or as a temporary
trapping center is determined by the ratio of the rate constants (d) to
(e) in the figure. The strength of coupling of the impurity with the
lattice depends on the form of the atomic states of the impurity near
the host lattice absorption edge, the greater the overlap the greater
the coupling. Variable valence also contributes to this coupling.

A number of contributed papers dealt with various aspects of the ideas
reviewed by Robbins. Stevels (Philips, Eindhoven) discussed energy trans-
fer in alkaline-earth aluminates activated with various rare-earth ions
and manganese. He described in detail the β-Al_2O_3, magnetoplumbite and
distorted magnetoplumbite structures, the first two of which have spinel
blocks but differ in the linking of these blocks in the crystal. In
β-Al_2O_3 most of the Mn^{+2} ions are at a short distance from the large
rare-earth-sensitizer cation that is situated between the spinel blocks;
consequently the ratio of probability of transfer of excitation energy
from the sensitizer to the manganese is approximately 50:1 compared to
the probability of the sensitizer emitting its own luminescent radiation.
In magnetoplumbite, most Mn^{+2} ions are at longer distances from the large
rare-earth-sensitizer cation, hence the probability of transfer of excita-
tion from the latter to the manganese is approximately equal to the proba-
bility of the sensitizer emitting its own luminescence. With the distorted
magnetoplumbite structure a small part of the Mn^{+2} ions are very near
to the large rare-earth-sensitizer cation, and for these the probability
of energy transfer to the manganese is 100 to 1.

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P.W. Tasker (AERE, Harwell) discussed the quenching of luminescence in semiconductors by charged dislocations. The electric fields around these dislocations can prevent the binding of the charge carrier to the activator, and the carriers then go on to recombine non-radiatively with carriers of opposite charge. Thus, within a small radius of a charged dislocation there can be no radiative activators. This effect could be seen in studies of the edge emission of ZnS samples excited in the scanning electron microscope (Jakobi, Hebrew Univ., Jerusalem).

The session on radiationless transitions, multiphonon emission, concentration quenching, and up and down conversion was led by a pair of talks by G. Blasse (Rijksuniversiteit, Utrecht) and R. Englman (Soreq Nuclear Research Center, Israel). Blasse's discussion centered around the well-known configuration coordinate diagram. He discussed the various possibilities when the curves for the lower and excited states were both parabolas with different parameters, and also the case when there was anharmonicity. Blasse's recipes for producing an efficient phosphor were (a) to look for systems in which the curves are not offset by much in configuration coordinate and (b) to use host lattices of high stiffness. The first recommendation is hardly an operational one, and therefore is rather unhelpful to the phosphor designer; at least it is no more helpful than other qualitative statements such as the need to obtain "energetic isolation" of activators from the host lattice. The second recommendation does not appear to correspond to a generally valid situation; efficient phosphors such as the various metal-activated alkali halides do not have particularly stiff lattices. The other theoretical treatments by Englman and C.W. Strutt (RCA, Princeton) seemed to underscore Blasse's opening quotation from Orbach that exact calculation is "hopeless" for many phonon processes and non-radiative processes.

A sequence of papers by the French contingent followed. N.C. Bourget (Université Claude Bernard de Lyon, Villeurbanne) described the strong temperature-dependence of quantum efficiency in $LaPO_4$:Ce,Tb due to the $^5D_3-^7F_5$ and $^5D_4-^7F_5$ transitions in Tb. There is a major increase in $Ce^{+3} \rightarrow Tb^{+3}$ transfer efficiency in the range 70-300 K. Bourget invoked thermally-activated $Ce^{+3}-Ce^{+3}$ transfer to account for this phenomenon. G. Boulon of the same institution described the transition from line to band emission from europium in $BaCaLa_2F_{10}$:Eu as a function of temperature and Ba/Ca ratio. His conclusion was that Eu on Ba sites gives only narrow lines. Mme. F. Gaume-Mahn (CNRS, Meudon) described the behavior of BaClF:Sm, which gives a red emission at room temperature and a yellow emission at low temperature.

P.J. Cresswell (School of Chemical Sciences, Univ. of East Anglia, Norwich) discussed upconversion in rare-earth Tm^{+3} in a calcium-sodium-yttrium chloride host. In this host upconversion can be obtained by pumping with 0.97 radiation, using Yb^{+3} as a sensitizer, but this involves a 3-step process. With Re^{+4} as a sensitizer, which has absorptions at

720 and 650 mμ, pumping can be accomplished at 647 mμ using an argon: krypton laser. This leads to two emissions from Tm^{+3} in the blue, a 450-460-mμ band and a 480-mμ band. The slope of the intensity vs laser power curve is 2 in this case. The efficiency is low because of the host material used, and Cresswell indicated that a better host would be needed for practical applications.

F. Auzel (CNET, Bagneux) attempted to predict upconversion using Yb^{+3} to Tm^{+3} in other than fluoride-type host lattices. He assumed that the oscillator strength and the phonon coupling was the same from host to host and concluded that the fluorides are the best hosts. However, he stated these assumptions are such as to make these predictions of limited value.

A.G. Paulusz (GEC Hirst Research Centre, Wembley) dealt with the luminescence of nd° ions in fluorides. This luminescence is known in oxides, and the question is why is it not observed in the fluorides. Paulusz believes that the failure to observe it hitherto has been due to the fact that it is excited only at very high energies, namely, in the vacuum ultraviolet. His experiments with K_2TiF_6 and K_2SiF_4:10% Ti^{+4} (fired in anhydrous HF to suppress the yellow emission that one gets when the firing is done in air) suggested that his hypothesis was correct. Rough calculations show that the $F \rightarrow Ti^{+4}$ charge-transfer band should absorb at 1630-1780 Å, and that the emission should be at about 2500 Å. Although Paulusz's experimental arrangement did not allow him to examine the emission spectra, the excitation peaks that he found were in the appropriate region.

The point raised by Dean in his opening talk, the question of the phosphor surface, was the subject of the last invited presentation, by R.H. Williams (New University of Ulster, Coleraine) on the effects of phosphor surfaces on their performance. Since Williams was not a phosphor researcher but a surface physicist, the talk was essentially a tutorial on surfaces in general, what one should study about them, and what techniques are used. Most of his illustrations were chosen from semiconductors. In a contributed paper, Cyril Scott (Hull Univ.) discussed surface photovoltage spectroscopy, in which the depths of surface states can be measured by emptying filled surface states by illumination, measuring the contact potential difference between the semiconductor and the metal as a result. He illustrated this method with literature data on CdS which has absorbed oxygen from the air. He also pointed out that surface states could be filled as well as emptied by the light. The interpretation involved in this type of spectroscopy assumes that other things don't happen, such as excitation of electrons from the valence band in the barrier layer.

These presentations were followed by a general discussion of the existence of a "dead layer" in CR phosphors. It was pointed out that ZnO can give cathodoluminescence at very low voltages, well below 10 V. It seems singularly free of the "dead layer" that other phosphors display. The question was raised as to whether this "dead layer" was really a charging phenomenon rather than a layer of inert material. It was reported that one can get CR excitation of other phosphors at very low voltages when these materials are scrupulously clean on their surfaces. Also, Japanese workers have added conducting material to phosphors and were able to get cathodoluminescence at very low voltages.

The last programmed session concluded with very lively discussions provoked by blunt criticisms from A. Vecht (Thames Polytechnic, London) and P. W. Ranby (Thorn Lighting Ltd., Enfield) who chose to point out the important problems that the Conference had not addressed. Vecht made an extensive list of things that were not covered, including methods of phosphor preparation (solid state reactions vs precipitation reactions), the relationship of particle size and efficiency, the function of "fluxes" (both for charge compensation and crystal growth), and the question of economics of phosphors. He also inveighed strongly against *post facto* theoretical explanations which really didn't explain anything and were not useful in guiding the phosphor chemist. He twitted the academic community for concern with impractical systems, maintaining that the Science Research Council would underwrite research on any phosphor whose efficiency was less than 0.1%, but that it had no sympathy for research on efficient lamp or cathode-ray tube phosphors.

Ranby maintained that he had learned virtually nothing from the Conference and complained that the gap between real-life phosphor work and theory is getting too wide. He pointed out that halophosphate phosphors were not even mentioned at the meeting despite the fact that these phosphors are produced in tonnage lots for lamp manufacture. He reminded people of the health hazard of beryllium that was unsuspected by the lamp industry years ago and which ultimately led to the withdrawal of the zinc beryllium silicate lamp-phosphors and their replacement by the halophosphates. Ranby questioned whether there are any health problems associated with rare-earth activators that are now being so widely used.

The response of the theorists was initially very weak and apologetic but was gathering strength as the time came to adjourn for lunch. My own sympathies were divided between both communities. As indicated earlier, I had found much of the theory to be rather handwaving and qualitative, largely a more formal restatement of ideas that had long been known and put in simpler words. On the other hand, I could hardly go along with the view that a Europhysics Conference should be concerned with cost-reduction in phosphor manufacture and the potential health effects of the chemicals used in phosphors. It seems, alas, that even science is fractionated into two cultures.

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